CORROSION INHIBITION EFFECT OF EXTRACTS LEAVES OF *MOMORDICA DIOCIA* FOR IRON IN ACID MEDIA

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ABSTRACT

Strict environmental legislations and increasing ecological awareness among scientists have led to the development of "green" alternatives to mitigate corrosion. In the present work, literature on green corrosion inhibitors has been reviewed, and the salient features of our work on green corrosion inhibitors have been highlighted. Among the studied leaves, extract *Andrographis paniculata* showed better inhibition performance (98%) than the other leaves extract. *Strychnosnuxvomica* showed better inhibition (98%) than the other seed extracts. *Moringa oleifera* is reflected as a good corrosion inhibitor of mild steel in 1 M HCl with 98% inhibition efficiency among the studied fruits extract. *Bacopa monnieri* showed its maximum inhibition performance to be 95% at 600 ppm among the investigated stem extracts. All the reported plant extracts were found to inhibit the corrosion of mild steel in acid media.

KEY WORD: Corrosion, Inhibitor, Mild steel, Electrochemical, Synthesis.

INTRODUCTION

Among the several methods of corrosion control and prevention, the use of corrosion inhibitors is very popular (Abbas *et al.*, 2018). Most of the effective inhibitors are used to contain heteroatom such as O, N, and S and multiple bonds in their molecules through which they are adsorbed on the metal surface (Fouda *et al.*, 2018). The use of chemical inhibitors has been limited because of the environmental threat, recently, due to environmental regulations. These known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products as corrosion inhibitors (Ituen *et al.*, 2017). Plant products are organic in nature, and some of the constituents including tannins, organic and amino acids, alkaloids, and pigments are known to exhibit inhibiting action. Moreover, they can be extracted by simple procedures with low cost (Kumpawat *et al.*, 2012).

Carbon dioxide (CO_2) corrosion is one of the primary problems in oil and gas industry, costing billions of greenbacks every year (Jeengar *et al.*, 2013). Carbon dioxide corrosion has been of interest to researchers in oil industries for many years and there exists many theories about the mechanism of CO_2 corrosion (Mohammad *et al.*, 2018).

Many amines, steroids and alkaloids are derived from the flora which are rich in heteroatoms (N, O, S). mainly compounds containing heteroatoms show top inhibition studies (Sethi *et al.*, 2007 and Thiraviyan *et al.*, 2012).

Its many types range substantially inside the shape and bitterness of the fruit. bitter melon comes in a selection of sizes and styles. It additionally incorporates cytotoxic (ribosome- inactivating) proteins which includes momorcharin and momordin (Vishnuvardhanaraja *et al.*, 2003).

MATERIALS AND METHODS

Mild steel specimens of same composition with an exposed area of l sq.cm were used for potential dynamic polarization and AC impedance measurements.

All the three additives (S_1, S_2 and S_3) were preliminarily screened by weight loss method. The metal specimens were initially weighed prior to immersion in 1M H_2SO_4 and 1M HCl as corrodant.

After a period of 1 hour, the specimens were removed, washed with water, dried and weighed to an accuracy of four decimals. From the initial and final masses of the specimen (before and after immersion in the solution) the loss in weight was calculated. The experiment was repeated for various inhibitor concentrations (0.5mM-8mM) in 1M H_2SO_4 1M HCl and 0.5M H_2SO_4.

To study the effect of temperature the above procedure was carried out at different temperature ranges 40 °C-60 °C using thermostat. Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit (ACM Gill instrument model 903). A platinum foil and Hg | $HgSO_4$ | 1N H_2SO_4 electrode were used as auxiliary and reference electrode, respectively. Double layer capacitance and charge transfer resistance value were obtained using AC impedance measurements.

Synthesis of Inhibitors

Synthesis of r-2, c-6-diphenylpiperidin-4-one semicarbazone (S₁)

The method of Balasubramaniam and Padma10 was followed for the preparation of the compound r-2, c-6-diphenylpiperidin-4-one (P1). To the solution of r-2, c-6-diphenylpiperidin-4-one (1.2g in 15 ml ethanol), ethanolic solution of semicarbide hydrochloride (0.5g) and sodium acetate (0.5g) were added. The resulting mixture was stirred by use of magnetic stirrer till the precipitate was formed. The product formed was filtered off and washed with water. Crystallization from ethanol gave 62% yield with an m.pt range of 176-178 °C.

Synthesis of r-2, c-6-diphenyl-t-3-ethylpiperidin-4-one semicarbazone (S₂)

Preparation of r-2,c-6-diphenyl-t-3-ethylpiperidin-4-one (P2) was prepared according to the procedure of Noller and Baliah11. Ethanolic solution of Semicarbazide hydrochloride(0.5g) and sodium acetate (0.5g) were added to r-2, c-6-diphenyl-t-3-ethylpiperidin-4-one (1.5g in ethanol). The contents of the flask were shaken well for 15 minutes and kept at room temperature overnight. The product formed was filtered, washed and recrystallized from ethanol with yield 52% and m.pt range 184-186⁰C

Synthesis of r-2, c-6-diphenyl-t-3-isopropyl-piperidin-4-one semicarbazone (S₃)

The procedure given by Noller and Baliah11 was followed for the synthesis of r-2, c-6-diphenyl-t-3-isopropylpiperidin-4-one The method used for the synthesis of S_2 is adopted for the synthesis of S3 with yield 56% and m.pt 191-193 °C.

Corrosion Monitoring Techniques Used

There are basically two general class of corrosion monitoring techniques. They are physico-chemical methods and electro chemical methods.

Electrochemical study

Electrochemical impedance spectroscopy (EIS) and Tafel polarization were conducted in an electrochemical measurement unit (ACM Gill instrument, model, 903). The EIS measurements were made at corrosion potentials over a frequency range of 10 KHz to 0.01Hz with single amplitude of 10mV. The Tafel polarization measurements were made after EIS studies for a potential range of -200 mV to +200mV with respect to open circuit potential, at a scan rate of 1mV per sec. the Icorr, Ecorr, Rt and Cdl values were obtained from the data using the corresponding Corr view and Z view software's.

The synergistic effect was studied by the addition of 1mm KI and 1mm H_2SO_4 containing various concentrations of the inhibitors S_1, S_2 and S_3 for the duration of 1 hour. From the weight loss the corrosion rate and inhibition efficiency was calculated.

RESULTS AND DISCUSSION

The synthesized compounds (Fig. 1) were characterized by elemental analysis (Table 1), IR, NMR and 13C NMR spectral studies. Analysis of the IR spectra of the compounds S_1, S_2 and S_3 indicates that all the compounds show two strong bands in the regions 3525-3398cm⁻¹ and 3400-3367 cm⁻¹ assignable to vasym (N-H) and vsym (N-H), respectively of the -N_4H_2 group of the compounds' 12, 13. Another medium intensity broad band around 3319-3306 cm⁻¹ found in the IR spectra of these compounds is due to —NH stretching vibration involving ring nitrogen. Bands appearing in the region 3100-3030 cm⁻¹, 2975-2950 cm⁻¹ and 2898- 2850cm⁻¹ are due to aromatic v(C-H), aliphatic and alicyclic vasym(C-H) and aliphatic and alicyclic vsym(C-H) respectively. A medium to sharp band observed in the region 1568-1492cm⁻¹ is attributed to v(C=N) stretching 14 which indicate the presence of azomethine group in the compound. A strong band

in the region 1720-1680cm^{-1} is mainly due to C=O stretching mode 15. In addition several other bands in the region 1450-900cm^{-1} can be attributed to vibrations involving interactions between C=O stretching and C-N stretching (Table 2).
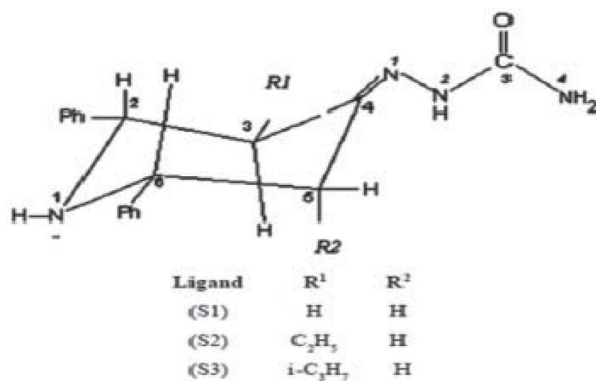

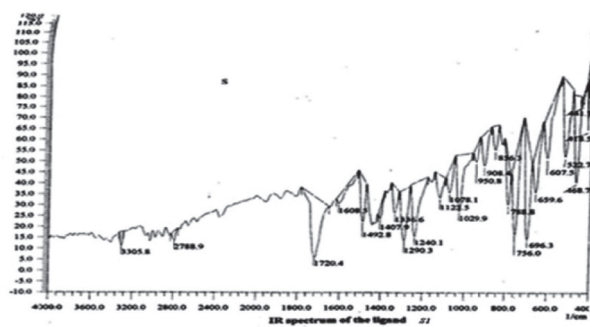**Fig. 1.** Structures of the Compounds S$_1$, S$_2$ and S$_3$

Fig. 2. IR Spectra of the ligand S1.

1H NMR Spectral Studies

The N-H proton of piper done ring system usually exhibits singlet in the region 2.00-2.07 ppm 16. The compound S$_1$ shows a singlet at 2.1 ppm is assignable to N-H of piperidin-4-one semi Cabazon. All the compounds exhibit a singlet in the region 8.6-8.8ppm is due to =N-NH proton. The —CoNH$_2$ group of the compounds give two broad signals ~5.3 and ~6.3ppm. The presence of these broad peaks indicates the two protons are nonequivalent and this may be due to restricted rotation of —CoNH$_2$ bond as a result of orientation of semi Cabazon group in space. All the compounds show multiple between 7.24-7.61 ppm which is due to aromatic protons (Fig 1b & Table 3).
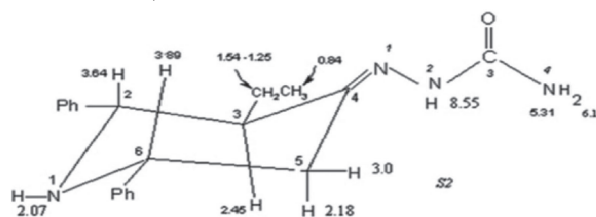

Fig. 3. H1chemical shift data (ppm) S$_2$.

NO$_{13}$C NMR Spectral Studies

The 13C NMR spectral data of the ligands (S1,S2 and S3) are given in the Fig 4 & Table 4. The signals in the range 150-152.5 ppm is assigned to the azomethine carbon (C=N)17. The signal in the range 126-145 ppm 18, 19 is due to aromatic carbon. The signals of the carbon atom of heterocyclic ring occur in the range 36-69 ppm. Thus, IR, 1H NMR Spectral studies and 13C NMR Spectral studies confirm that the ligands (S$_1$, S$_2$ and S$_3$) exist in chair confirmation with alkyl and phenyl groups in equatorial orientation and that they exist in keto form rather than enol form.

Weight loss studies

The tested piperidin-4-one semicarbazones inhibited

Table 1. Physical and analytical data of 2,-6-diphenylpiperidin-4-one semicarbazones.
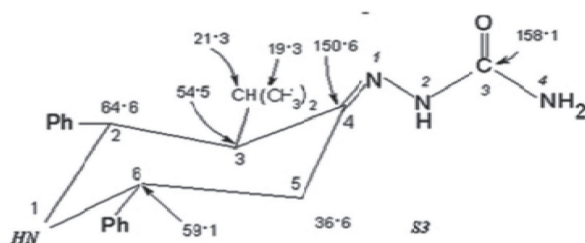
S. No .	Ligands Molecular Formula	Melting Point (ºC)	Yield (%)	Elements Found (Cale)		
				C (%)	H (%)	N (%)
(S$_1$)	C$_{18}$H$_{20}$N$_4$O	178-180º	65	70.20 (70.09)	6.29 (6.54)	18.01 (18.18)
(S$_2$)	C$_{20}$H$_{24}$N$_4$O	190-192º	70	71.22 (71.39)	7.03 (7.19)	16.52 (16.66)
(S$_3$)	C$_{21}$H$_{26}$N$_4$O	186-188º	65	71.39 (71.96)	7.62 (7.48)	16.04 (15.99)

Table 2. Important IR absorption bands of compounds S$_1$, S$_2$ and S$_3$

Compound	V (C=O)	V (N$_4$-H)	V (N$_4$H)	V (N$_4$-H)	V (N$_2$-H)	V (C=N)
S$_1$	1724s	3306s	3398m	3367m	3085m	1492m
S$_2$	1682s	3319m	3525s	3406s	3186s	1558s
S$_3$	1680s	3317m	3525s	3408s	3192s	1555s

Table 3. 1H NMR Chemical shift data (ppm) S_1, S_2 and S_3

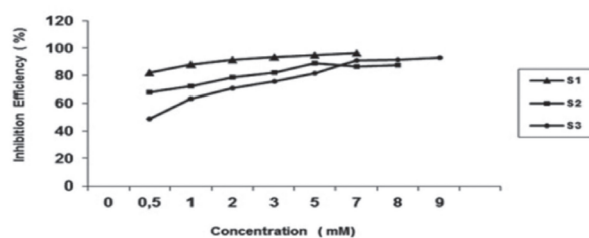| Ligaud	H-2	H-3		H-5		H-6	Aromanc protous	Ring N-H	- CONH	=NNH	Other Protons
		1I	eq	1I	eq						
(L)	3.31 co J=11.3	1.93 (dd I=14.12)	2.52 (0)	236-2.42(m)		3.75dd J=11.3	7.2-7.48 (m.10H)	6.2(b)	5.24b 6.26b	8.85(s)	......
(L)	3.64 (J=10)	2.45 (tJ=11	2.118 (ddJ=11.8)	3.0 (ddJ=13.	3.9(6d,s= 1.9	7.24-7.46 11.4,2,4	(m.10H)	2.07	5.34(b) (s)	8.55(s) 6.15(b)	1.25.154 (m.2H c-3-CHCH 0.88(t3t c-3-CH, CH,)
(L)	3.37 dJ=3.10	2.39 (dJ=11)	2.06(dd J=14.9. 11.5)	3.04(dd J=11. 5.3.2)	3.86 (ddJ=11 1.7)	7.28-7.44 (m.10H)	2.03 (s)		5.42 (b), 6.1 (b)	8.77 (s)	

Fig. 4. 13C NMR Chemical shift data (ppm) S_3

Fig. 5. Variation of inhibition efficiency with concentration of inhibitors at room temperature in 1M H_2SO_4
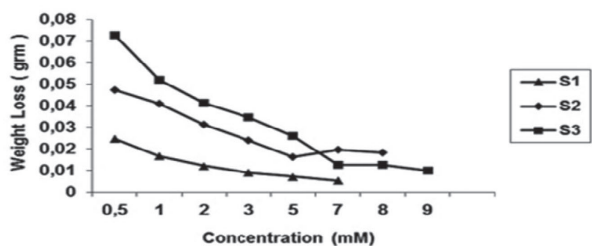
Fig. 6. Plot of Weight loss (gms) *vs* concentration (mm) for Inhibition of corrosion of mild steel in 1M H_2SO_4

the corrosion of mild steel even at low concentration of the acid (1M H_2SO_4) at room temperature. The inhibition efficiency was found to increase with increasing inhibitor concentration. The maximum efficiency of about 88-96% was obtained at concentrations of 5 mm-8 mm of inhibitors (Tables 5) and is depicted in Fig. 5. It is observed that all the three compounds inhibit the corrosion of mild steel at all concentrations used in this study. A plot of weight loss versus inhibitor concentration (Fig. 6) reveals that the metal loss and corrosion rate (mpy) progressively decreased with increasing inhibitor concentration as is evident from Table 5.

Corrosion rate in 1M H_2SO_4 for various concentrations of the inhibitors (S_1, S_2 and S_3) was determi. The ned after 1hour of immersion. The corrosion rate expressed decreased with increasing inhibitor concentration as evident from Tables 5 and Fig. 7.

CONCLUSION

According to experimental and theoretical findings, it could be concluded that:

1. CBIPM is a good corrosion inhibitor for mild steel in 1.0 M HCl solution and its inhibition efficiency depends on its concentration.

Table 4. 13C NMR Chemical shift data (ppm) S_1, S_2 and S_3.

Ligand	C-2	C-3	C-4	C-5	C-6	-CH₁	- CH₁	-CH	-(C=O_	Arpmabc carbons
(S_1)	69.2	44.6	152.1	36.4	60.4	—	—	–	158.4	127.2,127.5,127.8, 143.9,144.6
(S_2)	67.4	51.3	150.8	36.3	60.5	12.5	19.3	—	158.3	126.6,127.3,127.4 128.5,128.6,143.8,144.6
(S_3)	64.6	55.5	150.6	36.6	59.1	19.3	—	21.3	158.1	127.2,127.5,127.7,128.4, 128.6,128.7,144.7,144.9

Name of the inhibitor	Intubitor Concen (mM)	Weight Loss (gms)	Inhibiyion Efficiency (%)	Corrosion Rate (mpy)	Degree of Coverage
S1	Blank	0.1375	18826.5		
	0.5	0.0245	82.18	3354.54	0.8218
	1	0.0167	87.85	2286.56	0.8785
	2	0.0121	91.2	1656.73	0.9120
	3	0.0089	93.52	1218.58	0.9352
	5	0.0071	94.83	972.13	0.9483
	7	0.0053	96.14	725.67	0.9614
S_2	Blank	0.1463	20031.39		
	0.5	0.0472	67.73	6462.62	0.6773
	1	0.0408	72.11	5586.33	0.7211
	2	0.0313	78.6	4285.59	0.7860
	3	0.0353	75.8	4833.27	0.7580
	5	0.0164	88.79	2245.48	0.8879
	7	0.0195	86.67	2669.94	0.8667
	8	0.0184	87.23	2519.32	0.8723
S_3	Blank	0.1413	19346.79		
	0.5	0.0725	48.69	9926.70	0.4869
	1	0.052	63.19	7119.84	0.6319
	2	0.0414	70.70	5668.48	0.7070
	3	0.0345	75.58	4723.74	0.7558
	5	0.0258	81.74	3532.53	0.8174
	7	0.0127	91.01	1738.88	0.9101
	8	0.0125	91.15	1711.50	0.9115
	9	0.01	92.92	1369.20	0.9292

2. Potentialdynamic polarization curves indicated that CBIPM acts as a mixed type inhibitor.
3. EIS plots indicated that Rct values increase and Cdl values decrease with inhibitor concentration.
4. The UV-vis spectroscopic study clearly reveals the formation of Fe-CBIPM complex, which may be also responsible for the observed inhibition.
5. The theoretical results were found to be consistent with the experimental results for the corrosion inhibition of mild steel by the CBIPM inhibitor, Salari M. Corrosion inhibition of stainless steel 302 by 1-methyl-3-pyridine- 2-Yl-thiourea in acidic media.

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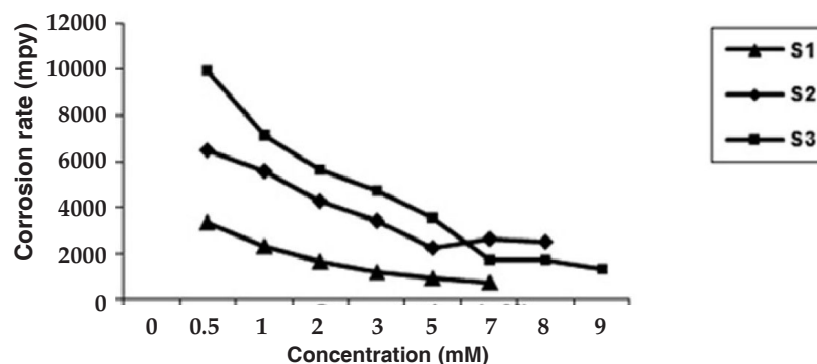
Fig. 7. Variation of Corrosion rate as function of concentration of inhibitors for the corrosion of mild steel in 1M H_2SO_4

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